Potato starch stabilized synthetic latexes

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CHAPTER 3

A systematic study on synthesis and properties of polyvinyl acetate latexes stabilized by pyrodextrinated potato starch

Abstract

The influence of the level of pyrodextrination of potato starch on the performance as a protective colloid for polyvinyl acetate latexes was investigated systematically. A simplified Taguchi design of experiments was used to investigate the influence of several different process variables of the pyrodextrins preparation process (namely amount of added hydrochloric acid (HCl = 15, 18 and 21 mmol/kg starch), level of pre-drying (PDM = 15, 30 and 45 minutes at 90°C), dextrination time (DTH = 3, 5 and 7 hours at 160°C)) on the final properties of the pyrodextrins. The pyrodextrination process appears to be controlled by the factors HCl and DTH mainly. The variation in reaction conditions resulted in pyrodextrins with distinct differences in colouration and viscosity level.

The protective colloid properties of the pyrodextrins were evaluated in vinyl acetate free-radical polymerization. All latexes were generated with the same polymerization procedure and showed similar monomer conversion levels and dry matter recoveries above 97 wt %. The process variables used during pyrodextrination only had a limited influence on the glass transition temperature of the latexes prepared. However, other process and product composition related variables (e.g. power consumption, conversion, recovery and grafting) show pronounced differences that can be related to the pyrodextrination process factors HCl and DTH mainly. Latexes with a monodisperse particle size distribution require a higher energy input during processing than their polydisperse counterparts.

Introduction

The commercial application of (pyro)dextrins as protective colloids in free radical polymerizations dates back to at least five decades. However, it still constitutes a relevant research topic, at least at industrial level, as testified by the number of publications in the recent past [1-9]. Polyvinyl acetate (pVAc) latexes stabilized with pyrodextrins are suitable for formulating (re-moistenable) adhesives characterized by dry matter contents up to 70 wt%. Pyrodextrins can be applied in two different ways in emulsion polymerization, i.e. either by adding the total amount before or partly after the polymerization reaction. Latexes with similar properties can be produced in both ways and also with different types of pyrodextrins.

The principle of pyrodextrination involves a pre-defined level of acidification of a starch source, moisture removal and exposure to heat [10]. Acidic hydrolysis and transglycosylation are believed to be the most important mechanisms for changing the structure of starch during pyrodextrination, both resulting in relatively small starch fragments with a high level of branching [11-15]. The colouration of starch during a pyrodextrination process is associated with the formation of conjugated double bonds, which can be generated in carbohydrates by dehydration of the carbohydrate moieties and aldol additions/condensations. The amount of reducing sugars increases with the extent of starch hydrolysis, with the subsequent dehydration resulting in hydroxyl methyl furfural (HMF) or related structures (Figure 1). HMF can be converted into other compounds at hydrothermal conditions (Figure 2).

The intermediate 2,5-dioxo-6-hydroxy-hexanal contains α-hydrogens, next to a carbonyl group, and is believed to form complex polymers by aldol addition/condensation. The polymers formed are called humins and are characterized by a relatively high amount of conjugated double bonds [16-18]. Caramelization can occur at pyrodextrination conditions as well and this reaction also results in starch with conjugated double bonds [19-22].

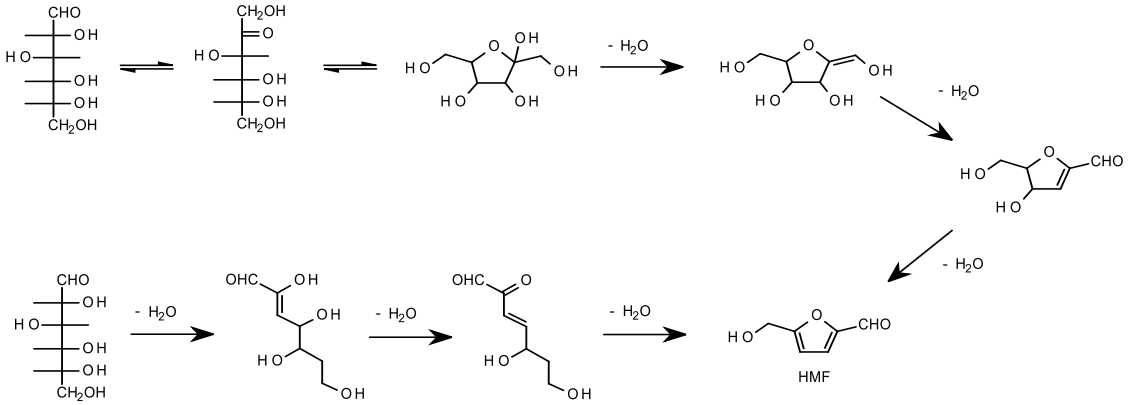


Figure 1: The two proposed patterns for the conversion of glucose into HMF by dehydration [16].

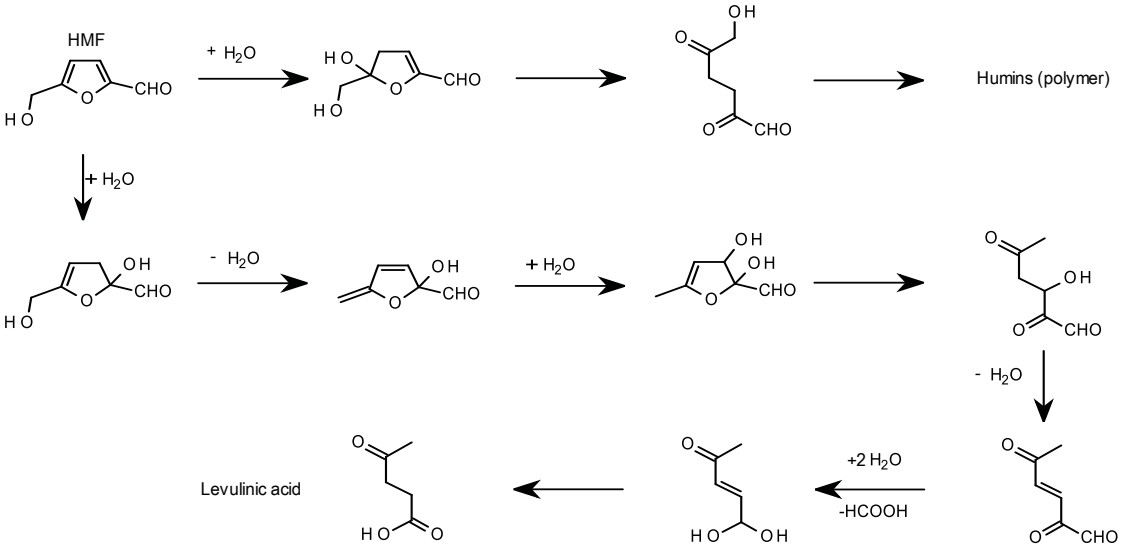


Figure 2: Proposed reaction mechanism for the conversion of HMF into humins and levulinic acid [17].

Starch becomes yellow when exposed to pyrodextrination conditions and this colouration is related to a change in the amount of conjugated double bonds. The latter is associated with radical scavenging properties and could therefore have a considerable impact on the efficiency of a free radical polymerization process [23]. Therefore, pyrodextrins with a lower degree of yellowness are preferred if there is a choice between pyrodextrins with similar intrinsic viscosities and different levels of yellowness (Figure 3) [20]. The intrinsic viscosity [η] is a measure of a solute's contribution to the viscosity of a solution (Equation 1) [24]:

Equation1:
$$[\eta] = \lim_{c \to 0} \frac{\eta_{sp}}{c}$$

where c denotes the concentration of the dissolved polymer and η_{sp} stands for specific viscosity of the solution. The latter can be calculated from the actual viscosity of the solution (η) and the viscosity of the pure solvent (η_0) (Equation 2) [24]:

Equation 2:
$$\eta_{sp} = \frac{(\eta - \eta_0)}{\eta_0}$$

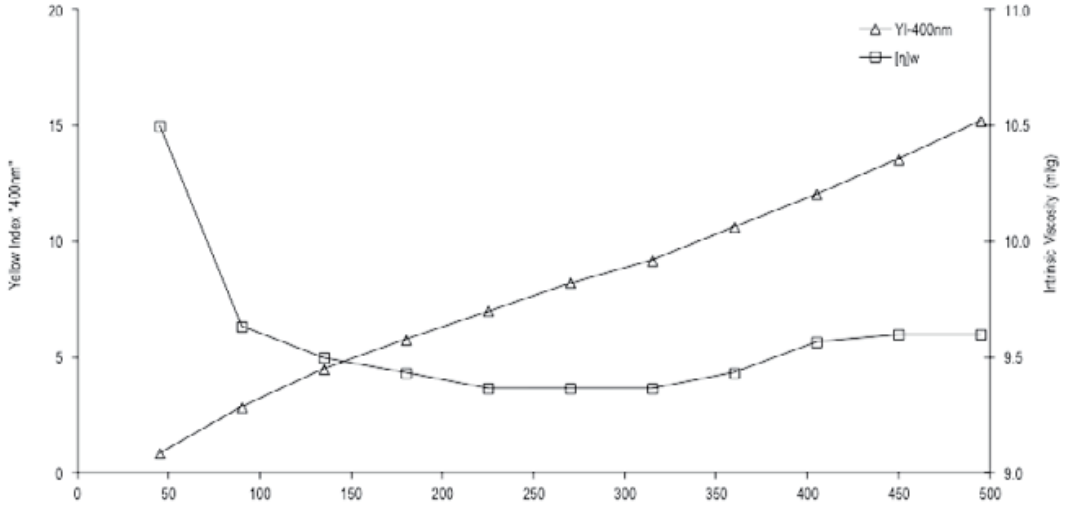
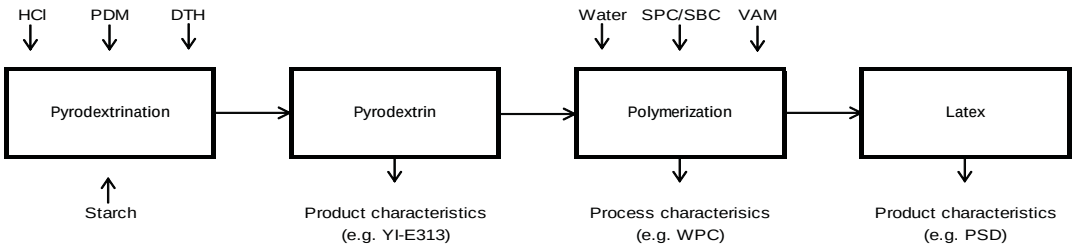


Figure 3: Yellow index 400nm (YI-400 nm) and the weight average of [η] as function of derivatization time [20].

Pyrodextrins used as protective colloids are usually intense yellow and can be quantified by the yellow Index E313 (YI-E313) [25]. However, the Commission Internationale de l'Eclairage (CIE) defined the L*a*b* colour space and this is a more discriminative approach for determining differences in colouration between pyrodextrins. This method relies on colour splitting into the components L* (black - white shift or intensity), a* (green - red shift) and b* (blue - yellow shift) respectively [26]. The pyrodextrination also has a considerable impact on the level of viscosity of the product after dissolution. Changes in viscosity, of either pyrodextrins in water or the final latex, can be measured by absolute (e.g. dynamic rotational; Brookfield) or kinematic (e.g. flow through an orifice; Ostwald) based viscometers and the latter is typically ten times more precise then the former [27]. Differences in amount of hydrocholoric acid (HCl) present in the pyrodextrin might be of influence on the polymerization reaction as well. Moreover, changes in pH and ionic strength can influence the radical and particle formation process and chloride is reported as a radical scavenger [28-29].

The demand of more sustainable products is steadily increasing and the general rules of green chemistry and engineering are useful guidelines to improve current production processes and products [30-32]. Pyrodextrination and free radical polymerizations are both flexible production processes with respect to changes in reaction conditions (e.g. processing temperature and reagent concentrations), but characterized by high processing temperatures for common free radical polymerizations (i.e. 50 to 80 °C) and even higher processing temperatures for pyrodextrination (i.e 75 to 250 °C) [2,10]. Pyrodextrins can be prepared by low reaction temperatures, but the corresponding products are believed to be less suitable as protective colloid in free radical polymerizations. The level of cold water solubility of the pyrodextrin is usually proportional to the total heat exposure and a change of this variable might introduce problems during polymerization and/or application if no precautions are taken [10]. Systematic studies on the impact of the processing conditions on the pyrodextrins performance as protective colloids is lacking in the open literature despite the fact that it is an absolute necessity for proper optimization of pyrodextrin stabilized pVAc latexes.

In this study, a typical pyrodextrination process for preparing a product with protective colloid characteristics was selected and the process parameters pre-drying (PDM), hydrochloric acid (HCl) and dextrination time (DTH) were varied to generate pyrodextrins with different structures and properties. The obtained pyrodextrins were used as a protective colloid in a vinyl acetate monomer (VAM) based polymerization. Sodium persulfate (SPS) was mainly used in thermal dissociation mode and the pH was kept in the range of 5 – 7 during polymerization with the help of sodium bicarbonate (SBC). Remnant SPS was converted by sodium thiosulfate (STS) after the polymerization was finished. The impact of the applied changes on process and product characteristics was evaluated. The general strategy is depicted in Scheme 1.
The overall process consists of two steps, i.e. pyrodextrination and polymerization processes. These can be in principle statistically analyzed in an independent manner, but it is also possible to link the pyrodextrin variables HCl, PDM and DTH directly to the process and product characteristics of the latex. The latter does not require extensive characterization of the pyrodextrins used, and this is desirable due to their very complex chemical nature, and only demands a fixed latex preparation procedure. This integrative approach, where the input variables of the pyrodextrination are statistically related to the process and product characteristics, besides its novelty, is preferred and also used in the present work.



Scheme 1: General depiction of the process steps, and most important variables, involved for making a pyrodextrin stabilized pVAc latex (WPC = Water bath power consumption and PSD = particle size distribution).

Experimental

Materials

The potato starch used in this study is commercially available under the trade name Potato starch Food grade (AVEBE U.A). The vinyl acetate monomer (VAM) was purchased from ACROS and contains 3-30 ppm hydroquinone. Analytical reagent grade sodium persulfate (SPS) was supplied by VWR International. Hydrochloric acid (HCl), Sodium bicarbonate (SBC) and sodium thiosulfate pentahydrate (STS) were of pro analyse quality and were purchased from Merck. All ingredients were used without additional purification and the solvent was demineralised water in all cases.

Pyrodextrination of starch

1 kg potato starch (20 wt% moisture) was placed in the bowl of a Hobart mixer. A given amount of HCl (L = 15 mmol; C = 18 mmol and H = 21 mmol) was dissolved in 160 ml demi-water and then slowly added to the starch during mixing. The obtained mixture was stored for 16 hours at 8°C in a closed plastic bag. The mixture was then pre-dryed twice in a Retch

fluid bed dryer for 60 minutes at 60°C and for several minutes at 90 °C (L = 15 minutes; C = 30 minutes and H = 45 minutes) and immediately added to a rotating reactor with a constant temperature of 160°C. The product was removed from the reactor at x hours after addition (L = 3 hours; C = 5 hours and H = 7 hours) and stored at room temperature in a plastic bag after cooling down on a piece of paper for 2 hours.

Experimental design

A Taguchi L8 orthogonal design allows the evaluation of the three factors (i.e. HCl, PDM and DTH) and their interactions [9]. The effect of a factor, or an interaction, is in the simplified Taguchi method calculated by multiplying the measured value with the corresponding number in the Taguchi L8 matrix (Table 1). The effect of a factor, or an interaction, is defined as the sum of the obtained values of the eight runs performed after this multiplication. The Taguchi L8 design was augmented with a centre point (C). This setting was executed in triplicate in order to get an impression of the overall level of noise in the pyrodextrination procedure [9,33].

Table 1: Taguchi L8 matrix for three factors and their interactions.

Run	Code	Factors or interactions						
		A_T	B_T	A_TB_T	C_T	A_TC_T	B_TC_T	$A_TB_TC_T$
1	LLL	-1	-1	-1	-1	-1	-1	-1
2	LLH	-1	-1	-1	1	1	1	1
3	LHL	-1	1	1	-1	-1	1	1
4	LHH	-1	1	1	1	1	-1	-1
5	HLL	1	-1	1	-1	1	-1	1
6	HLH	1	-1	1	1	-1	1	-1
7	HHL	1	1	-1	-1	1	1	-1
8	HHH	1	1	-1	1	-1	-1	1

Polymerization equipment

A double-jacketed stainless steel (316) reactor (1 l) equipped with a stainless steel (316) spiral ribbon stirrer (2 cycles) with a width of 1 cm and an outer dimension of 10.5x7 cm (height x diameter)) was used. A lid made of borosilicate glass with several connection points was placed on top and the reactor was completely insulated with radiator foil. A reflux cooler was placed on top together with a pt-100 probe for measuring the temperature of the headspace in the reactor (HST). The feeding lines of VAM and the SPS/SBC mixture were placed outside the reflux region with the aid of an accessory to minimize the contamination of VAM with water and premature dissociation of SPS (Figure 4).

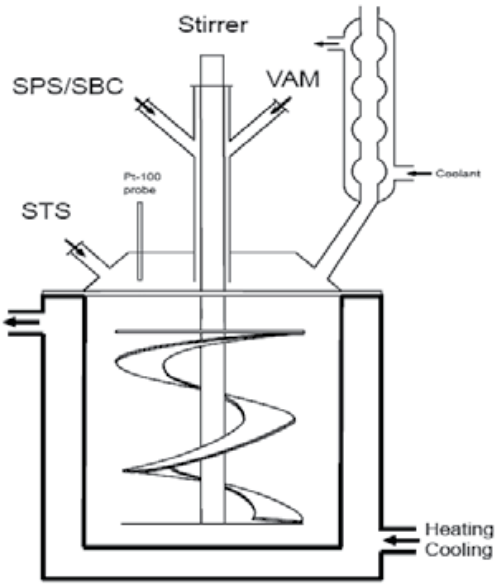


Figure 4: Schematic representation of the polymerization reactor used.

VAM was dosed with a peristaltic pump equipped with polytetrafluoroethylene tubing (4 mm) and the volume removed from the storage bottle was replaced by dry nitrogen. The actual VAM dosage was also monitored with a balance. One syringe pump was used to add a premix of SPS and SBC in water and another syringe pump was used to add STS in water after the actual polymerization was finished.

Polymerization procedure

The polymerization reactor was filled with 257.5-258.1 g of demineralized water and 33.8-34.4 g of a potato starch based pyrodextrin (moisture content: 1.1-2.9 wt %) was added to reach a pyrodextrin concentration of 10 wt % (with respect to the water amount) in the final latex. Automatic mixing (0-0.75 hours: 240 RPM; 0.75-9.0 hours: 120 RPM) was started after one minute of gentle manual homogenization. The applied temperature profile and dosage protocols of VAM, SPS/SBC and STS are given in Figure 5. VAM was used without inhibitor removal in order to closely resemble experimental conditions applicable at industrial scale. A total of 200 g VAM was added in all cases with a pre-dosage of 15 g VAM. The actual dosage was monitored in time and the total amount of VAM added was used for mass balance calculations. 1.5 g SPS and 2.0 g SBC were dissolved together in 46.5 g demineralised water and 30.5 ml of this mixture was added during the polymerization. The actual addition started after 104 minutes with a pre-dosage of 5 ml (5 ml/minutes) followed by 25.5 ml with a dosage speed of 5.8 ml/hour. The reducing agent was 0.3 mM STS and 3 ml was added with 3 ml/hour after 7.5 hours after the preparation procedure was started.

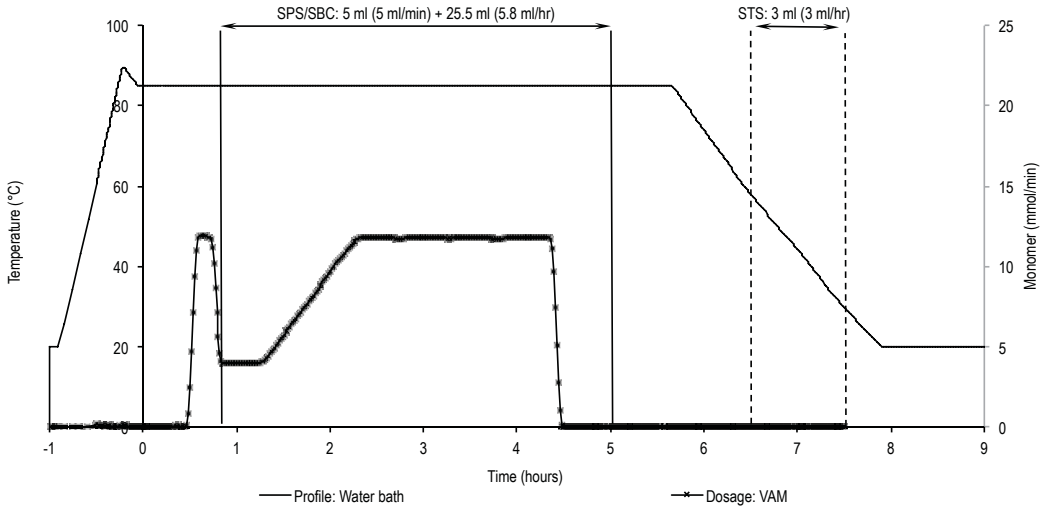


Figure 5: Applied temperature profile and dosage protocols of VAM, SPS/SBC and STS.

Characterization of pyrodextrins and corresponding latexes

A Datacolor Spectraflash SF-450 was used to determine the colour of the pyrodextrins after complete dissolution in water (concentration 4 wt %; demi water; settings: illuminator, D_{65}; 10°; spectrum, 360–700 nm; mode, transmission/absorption). The Ostwald viscosity was determined by measurement of a solution with 58% refraction at 25°C.

The WPC is expressed in a percentage in the range of -100 to 100 % and this value was recorded every 3 seconds during the preparation procedure. The amount of water present in the water bath was approximately the same in each experiment in order to minimize the variation between the executed experiments. The average WPC of 0-0.5 hours was calculated and defined as the heat loss to the environment. This value was subtracted from all recorded values before the sum was taken from all the readings in the period from 0-7 hours. The obtained value was used as a measure for the WPC during polymerization

Viscosity, pH and dry matter of the obtained latexes were determined with the help of a Brookfield DV-II+(20RPM), WTW pH320 and Mettler Toledo PM100/LP16 (80 °C), respectively. Ethanal and residual VAM in the latexes were determined with a Perkin Elmer gas chromatograph equipped with a headspace sampling device, a Poraplot Q fused silica column (25 m x 0.32 mm) and a flame ionization detector. The gas chromatography measurement was performed on water diluted dispersions (10 wt %). About 2 ml of the diluted dispersion was centrifuged at 13 000 relative centrifugal force for 10 minutes and the supernatant was mixed 1:1 with 5 mM NaOH in water. This mixture was used to quantify the anion composition with a Dionex DX50 equipped with an ATC-1 ion trap, two Ionpac colomns (AS11-2 mm and AG11-2 mm) and an electrochemical detector. The separation of the different anions (sulfate, thiosulfate and free acetate) was achieved with a gradient of sodium hydroxide. PSD's were obtained with a Sympatec laser diffractor (LD) equipped with a Quixel wet dispenser and a Helos laser diffraction sensor (Range: 0.13-32.5 µm). The sample solution was circulated during measurement. Fraunhofer theory based calculations were used and the obtained particle size distributions are ISO 13320 compliant. Dynamic Light Scattering (DLS) measurements were performed with a Zetapals from Brookhaven (4 ml demi water and 2 drops of diluted latex (10 wt % in demi water); angle 90°; average of 10 measurements of 30 seconds). The amount of grafted (and/or complex mixture) material was determined based on a precipitation of 3-4 g

dispersion in 100 ml acetone (0-5 °C) followed by soxhlet extraction in acetone. The soxhlet extraction was automated with a Soxtec 2043/2046 system from Foss Analytical (Cellulose thimbles, 160°C; 6 hours boiling and 18 hours rinsing). The grafting efficiency (ϕ) is defined as:

Equation 3:
$$\phi = \frac{w_{pVAc}^{g}}{w_{pVAc}^{tot}} = \frac{w_{pVAc}^{g}}{w_{pVAc}^{g} + w_{pVAc}^{h}}$$

Where w_{pVAc}^{g} , w_{pVAc}^{tot} and w_{pVAc}^{h} denote the amount of grafted, total and homo-polymerized VAM. The grafted copolymer amount was simply taken as the dried residue after the acetone extraction. The total pVAc was calculated on the basis of the monomer intake and conversion values.

Glass transition temperatures (T_g) were derived from total heat flow and reversing heat flow curves determined with a modulated differential scanning calorimeter (mDSC) from TA Instruments (Q1000; 1 °C/min; amplitude: 0.5 °C; period: 60 s; large volume stainless steel pans; 20-50 mg dispersion was added to a pan without any preliminary handling steps).

Results

Pyrodextrin preparation

A Taguchi procedure was applied on the variables Ostwald viscosity, YI-E313 and CIE L*a*b*. The results of the CCC-pyrodextrin triplicate were used to estimate the level of variation. The effects of the three selected factors (HCl, PDM and DHT), and their interactions, which are larger than two times the standard deviation (σ) of the CCC, are shown in Table 2 (the original data is not shown for brevity).

The effect of the triple interaction is frequently used as an estimator of the level of noise in this type of experiments and therefore not evaluated. The reaction conditions for pyrodextrination had a pronounced impact on the (macro)molecular size of these products as testified by the relatively broad range of the Ostwald viscosity values (from 37 to 78 mPa·s). The corresponding modification mechanisms are controlled, according the simplified Taguchi calculations, by HCl, DTH and their interaction. These two factors control the acidic breakdown and transglycosylation [11-15]. This suggests that the pyrodextrination process is mainly controlled by these two molecular processes. Pronounced shifts in colouration (i.e. YI-E313, CIE L*, CIE a* or CIE b*) were observed as function of HCl and DTH and the impact of their interaction was smaller and in the opposite direction. The obtained results (i.e. magnitude and sign of the observed effects in Table 2) are in line with the fact that the viscosity and colouration are controlled by different processes. The variation in heat exposure introduced by the PDM procedure appears to be negligible with respect to DTH. The effect of PDM was not significant according the simplified Taguchi calculations and the interaction between DTH and PDM barely exceeds the level of noise calculated with the CCC setting. YI-E313 correlates with CIE b* (based on the sign of the coefficients in Table 2, columns 3 and 6) as expected because this parameter describes the blue - yellow shift of the colour analysed. CIE L* and a* show that the impact of the applied changes was not limited to the degree of yellowness only. The observed differences in colouration suggest that the applied settings did not only control the number of colouring groups generated during processing, but the type of colouring groups formed as well.

Table 2: Effect of different reaction conditions on the selected pyrodextrin variables based on Taguchi calculations (simplified). Only effects are shown which exceed two times the standard deviation (σ) of the triplicate of the CCC pyrodextrin.

Factors	Viscosity	Dextrin characteristics			
	Ostwald (mPa·s)	YI-E313	CIE L*	CIE a*	CIE b*
PDM	-	-	-	-	-
HCl	-26.3	10.1	-1.1	-1.2	6.3
PDM:HCl	-	-	-	-	-
DTH	-13.3	11.7	-0.9	-1.1	7.2
DTH:PDM	-	1.4	-0.3	-	0.9
DTH:HCl	-11.8	-1.9	0.5	-	-1.3
DTH:PDM:HCl	-	-	-	-	-
CCC (Average)	44.0	17.4	94.5	-2.0	10.3
CCC (2*σ)	0.4	1.1	0.1	0.1	0.7

Polymerization process characteristics

The selected VAM polymerization was executed with the CCC pyrodextrin and the profiles HST and WPC were plotted against time (Figure 6). The drop in HST to 66 °C at 0.5 hours was accompanied with an increase in the WPC. The sharp rise in the HST at ~4.5 hours coincided with a reduction in the WPC. This is indicative for a considerable level of refluxing of the binary azeotrope VAM and water mainly during VAM dosage. However, there is a considerable chance that azeotrope is contaminated with other ingredients of the reaction mixture (e.g. ethanal and acetic acid) [9]. The WPC was approximately 40 % during refluxing which was distinctly higher than the ~30 % when there was no VAM dosed and considerably lower than the maximum WPC possible. These characteristics offer a good starting point for evaluating the impact of different pyrodextrins on the WPC profile.

Polymerizations with the two pyrodextrins with highest degree of yellowness resulted in distinct WPC's (Figure 7). The obtained results were indicative for differences in level of refluxing and the composition of the products with YI-E313 ≈ 30 results apparently in a significant change in polymerization rate.

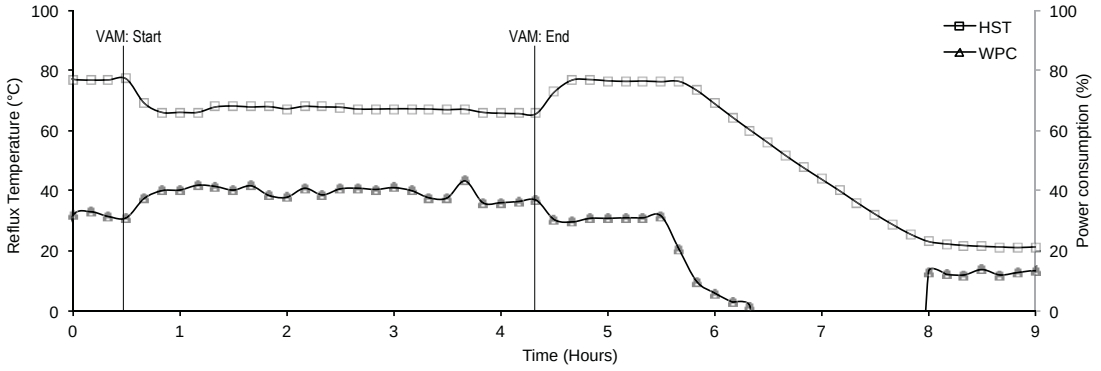


Figure 6: HST and WPC profiles of a VAM polymerization with the CCC pyrodextrin as protective colloid.

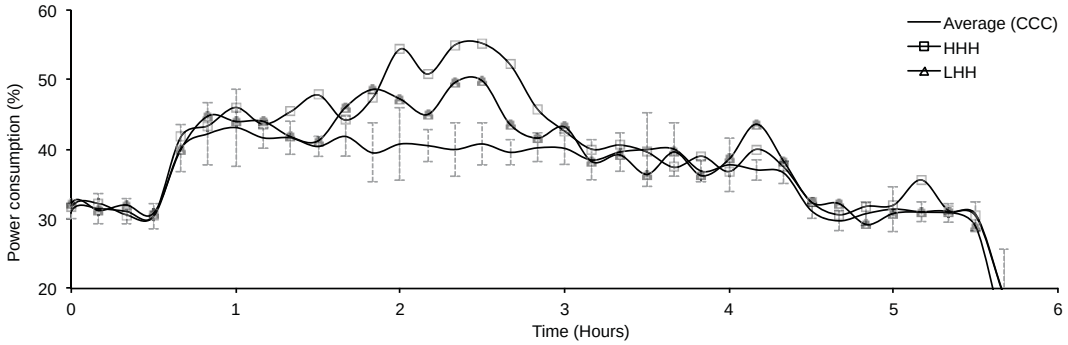


Figure 7: WPC profiles of the VAM polymerizations with the prepared pyrodextrins as protective colloid. The error bars represent the two times σ of the triplicate.

Simplified Taguchi L8 calculations were applied on the variables total WPC during polymerization, recovery, pH, residual ethanal, remnant VAM and amount of sulfate and thiosulfate ions. Two times σ of the CCC pyrodextrin protected latexes was used as a threshold value. The results of these calculations that exceed both thresholds are given in Table 3 (original values are not shown for brevity).

Table 3: Effect of the different pyrodextrins on the selected polymerization variables based on Taguchi calculations (simplified). Only effects are shown which exceed two times the σ of the triplicate of the CCC pyrodextrins.

Factors	WPC	Latex composition						
	Sum 0-7 hours (%)	Ethanal (mg/g)	VAM (mg/g)	Dry matter (%)	pH	Acetate (mmol)	Sulfate (mmol)	Thiosulfate (mmol)
PDM	-	-	-	-	-	-	-	-
HCl	31	-0.3	2.8	-0.8	0.07	2.57	-	0.04
PDM:HCl	-	-	-	-	-	-	-	-
DTH	26	-	1.6	-0.8	0.06	1.84	-	0.06
DTH:PDM	-	-	-	-	-	-	-	-
DTH:HCl	-28	-	-0.7	0.3	-	-	-	0.06
DTH:PDM:HCl	27	-	-	-	-	-	-	-0.05
CCC (Average)	131	1.4	6.0	98.6	4.97	36.02	3.33	0.34
CCC (2*σ)	19	0.2	0.4	0.1	0.02	1.44	0.14	0.02

The triple interactions were excluded from this evaluation. The total WPC during polymerization was affected in a significant way by the factors HCl and DTH. Both factors have, on their own and in combination, a pronounced influence on the variables residual vinyl acetate and YI-E313 (10.1, 11.7 and -1.9 respectively; Table 3). The total recovery of the latex was also distinctly influenced by the factors HCl and DTH and their interaction. The factors HCl and DTH need to be minimized for a quick and optimal polymerization process in general. The factor HCl did have a slight negative effect on the amount of residual ethanal of the latexes.

The differences in WPC during processing and residual VAM of the latex might be indicative for changes in the radical formation process. Unfortunately, the observed differences in pH and anion composition of the latexes were small and did not provide any confirming evidence. The observed variations in residual STS were close to the level of the triple interaction and therefore considered to be negligible. The amount of SPS at the moment that the STS solution was dosed was therefore comparable in all cases and the amount of sulfate generated during processing was close to the same as well.
Residual VAM and YI-E313 appear to be proportionally linked and this suggests that the pyrodextrin colouration had a distinct influence on the radical formation process. This assumption is plausible because an increase in YI-E313 is associated with an increase in conjugated double bonds and these types of bonds are known as radical scavengers [23]. However, chloride is a radical inhibitor as well and the fact that the chloride content of the pyrodextrins used is not the same in all cases makes deriving solid conclusions difficult [28,29]. The radical formation process is therefore influenced by either chloride content, colouration or a combination thereof. Differences were observed for pH and concentration acetate but they were small and can probably be related to the composition of the pyrodextrin and the amount of residual VAM respectively. From this it can then be concluded that HCl and DTH are essential for further optimization.

Latex characteristics

The factors DTH and HCl appear to be crucial for creating a pyrodextrin that is able to make latex with a monodisperse PSD (Figure 8). Only pyrodextrins prepared at the settings HHH and LHH generated PSD's that display a certain degree of monodispersity. The PSD's of the other latexes were similar to the PSD of the pyrodextrin prepared at the CCC setting and this latex was not monodisperse at all (Figure 8). The calculated variables from the above mentioned LD based PSD's were not suitable for Taguchi calculations. Therefore, DLS measurements at a 90° angle were used to determine the PSD of the latexes below 1 µm. The results are displayed in Table A1 together with the values of the latex viscosity and the T_g's based on Onset ($T_{g,onset}$), Inflection ($T_{g,inflection}$) and Endset ($T_{g,endset}$). However, Taguchi calculations (not shown for brevity) show that these three latex variables were barely influenced by the type of pyrodextrins used.
These considerations are on one side very positive since they clearly indicate the robustness of the process in the range of experimental conditions investigated. On the other hand, the lack of a strong correlation does not allow, at least for the thermal properties, identifying the experimental variables that can be used for further optimization.

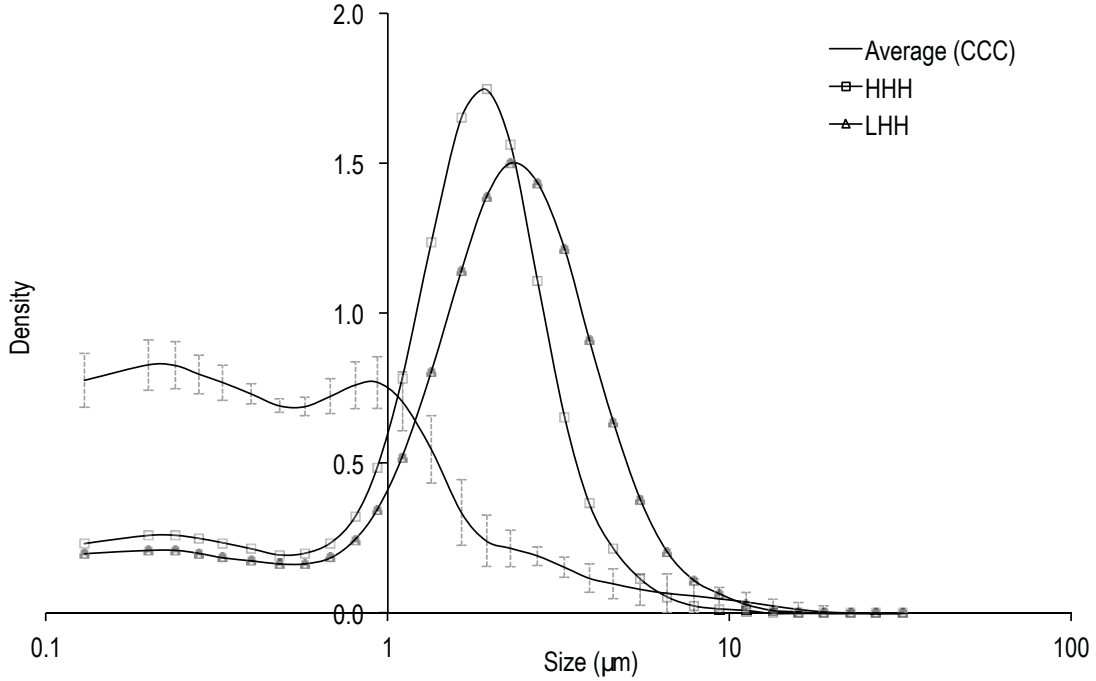


Figure 8: PSD's of a number of characteristic pyrodextrin based latexes. The error bars represent the two times σ of the triplicate.

Protective colloid related properties

The values for soluble and insoluble fractions from the acetone precipitation and extraction are given in Table A2 together with the calculated amounts of homopolymer, grafted polymer and ϕ. Table 4 shows the Taguchi calculations of the selected pyrodextrination conditions, and their interactions, which are larger than two times the standard deviation of the corresponding CCC pyrodextrin. An increase in HCl during the pyrodextrination resulted in a higher ϕ for the final latex, which can be partly attributed to differences in the HCl content of the pyrodextrins prepared. However, the HCl content in the pyrodextrin is only 0.1 wt % and the influence of variations in this area can therefore be ignored. The interaction between the factors DTH and HCl on the protective colloid properties of the corresponding pyrodextrins is remarkable. These latexes show a reduced level of grafting efficiency with respect to their counterparts based on CCC pyrodextrins but the level of monodispersity of the corresponding PSD's were considerably improved (Figure 8). Latex particles were more stabilized with this type of pyrodextrins apparently. Stabilization by a higher viscosity level of the water phase present during processing can be ruled out because the interaction of HCl and DHT resulted in a decrease in viscosity. The interaction also resulted in a lower degree of yellowing but the actual impact was small (Table 2).

The effect of the different pyrodextrins is not limited to the characteristics of the final latex only. There were distinct differences between the WPC profiles between polymerizations based on the pyrodextrins HHH and LHH and the other varieties (Figure 7), which was in turn strongly related to level of reflux of the azeotrope VAM and water. Pyrodextrins HHH and LHH might therefore induce significantly different reaction conditions during polymerization with respect to reaction temperature and amount of water (temporarily) withdrawn from the reaction mixture due to refluxing. Against this backdrop, the presence of several (statistically

significant) interaction coefficients between the different factors (Table 4) clearly indicated the complexity of the grafting reaction mechanism. These considerations render the use of a statistical procedure quite attractive for optimization at industrial level, but they also invite the thought (beyond the scope of the present work) of a more detailed study on the molecular mechanism.

Table 4: Effect of different reaction conditions on the selected pVAc composition variables (Table A2) based on Taguchi calculations (simplified). Only effects are shown which exceed two times σ of the triplicate of the CCC pyrodextrin.

Factors	pVAc composition		
	Homopolymer (mg/g)	Grafted polymer (mg/g)	ϕ (fraction)
PDM	-	-	-
HCl	-55	57	0.15
PDM:HCl	-	-	0.06
DTH	-25	24	0.07
DTH:PDM	-	-	-0.03
DTH:HCl	45	-45	-0.12
DTH:PDM:HCl	-	-	0.04
CCC: Average	269	96	0.24
CCC: 2*σ	24	23	0.02

Conclusions

The hydrochloric acid (HCl) content and the heat exposure time (DTH) constitute two crucial factors controlling not only the colour and viscosity of pyrodextrins, but also the protective colloid properties of these products. Heat flow during processing, monomer conversion, product recovery, anion concentration, pH, viscosity, particle size distribution, amount of grafted protective colloid and level of viscosity show distinct changes depending on the pyrodextrine used whilst the glass transition temperature remains approximately the same. The water bath power consumption during the latex preparation is proportional to the amount of HCl used during the pyrodextrination process, thus providing in principle a simple strategy to minimize the energy input for the latex synthesis. However, a high energy consuming polymerization procedure appears to be a necessity for creating a monodisperse particle size distributions. The performed statistical analysis is useful in identifying the interplay between the different investigated factors, indicating in some cases (e.g. grafting mechanism on molecular scale) the necessity of more dedicated studies. The selected reaction conditions for the pyrodextrination process do not reveal any straightforward strategies to create a latex with a monodisperse particle size distribution by reducing the amount of HCl used in the pyrodextrination. In this context, a significant change in pyrodextrination process and/or polymerization conditions is needed if this drawback needs to be solved. On the other hand, the employed statistical analysis reveals clearly the intimate relationship between the pyrodextrins synthesis and the properties of the polyvinyl acetate latex obtained by using them as protective colloid. To the best of our knowledge this represents a relevant novelty of the present work, clearly suggesting the need for more accurate macromolecular characterization if one wishes to establish a reliable structure-property relationship.

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Abbreviations

pVAc : Polyvinyl acetate.
HMF : Hydroxy methyl fufural.
YI-400nm: Yellow Index based on 400nm.
[η] : Intrinsic viscosity.
YI-E313 : Yellow Index based on CIE E313.
CIE : Commission Internationale de l'Eclairage.
CIE L* : Black - white shift or intensity (colour space)
CIE a* : Green - red shift (colour space)
CIE b* : Blue - yellow shift (colour space)
HCl : Hydrochloric acid.
PDM : Pre-drying in minutes.
DTH : Dextrination time in hours
VAM : Vinyl acetate monomer.
SPS: Sodium persulfate.
SBC: Sodium bicarbonate.
STS: Sodium thiosulfate.
HST: Headspace temperature.
WPC: Water bath power consumption.
PSD: Particle size distribution.
L : Low level.
H : High level.
C : Centre level.
A_T : PDM.
B_T : HCl.
C_T : DTH.
RPM : Revolutions per minute of stirrer.
LD: Laser diffractor.
DLS: Dynamic light scattering.
ϕ : Grafting efficiency.
w_{pVAc}^{g} : Amount of grafted pVAc.
w_{pVAc}^{tot} : Amount of total pVAc.
w_{pVAc}^{h} : Amount of homopolymer pVAc.
T_g : Glass transition temperature.
mDSC: Modulated diffential scanning calorimeter.
σ : Standard deviation.
$T_{g,onset}$: Onset point based glass transition temperature.
$T_{g,inflection}$: Inflection point based glass transition temperature.
$T_{g,endset}$: Endset point based glass transition temperature.
ΔT_g : $T_{g,endset} - T_{g,onset}$.

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Appendix

Table A1: Latex related variables: Viscosity, thermal transitions and DLS based variables .

Code	Viscosity	Thermal transitions (reversing heat flow)				PSD (DLS)	
		$T_{g,onset}$	$T_{g,inflection}$	$T_{g,endset}$	ΔT_g	Diameter	Half width
	(mPa·s)	(°C)	(°C)	(°C)	(°C)	(nm)	(nm)
LLL	40.0	12.3	14.1	16.5	4.2	254	53
LLH	36.0	12.0	14.0	16.0	4.1	236	62
LHL	34.0	10.8	13.8	15.8	5.0	240	82
LHH	32.0	10.7	12.4	14.6	3.9	249	64
HLL	40.0	12.0	13.9	15.7	3.8	253	63
HLH	36.0	11.3	13.4	15.4	4.1	239	70
HHL	34.0	10.8	13.0	14.7	3.9	240	45
HHH	32.0	10.4	13.4	15.3	4.9	239	68
CCC1	36.0	10.6	12.3	14.9	4.3	238	47
CCC2	34.0	10.9	12.8	14.7	3.8	237	53
CCC3	34.0	10.6	13.4	15.3	4.7	235	72

Table A2: pVAc composition variables and calculation of ϕ.

Code	Cold extraction		Hot extraction		pVAc composition				
	Insoluble pVAc (mg/g)	Soluble pVAc (%)	Precipitate cold precipitate (%)	pVAc in cold precipitate (mg/g)	pVAc total (mg/g)	Homo-polymer (mg/g)	grafted (mg/g)	ϕ (fraction)	Dry matter (mg/g)
LLL	229	202	31,4	72	364	274	91	0.25	431
LLH	203	227	31,6	64	365	291	75	0.20	429
LHL	273	161	24,5	67	370	228	142	0.38	434
LHH	292	133	17,6	51	366	184	182	0.50	425
HLL	244	187	24,4	60	366	246	119	0.33	431
HLH	229	199	30,8	71	364	270	94	0.26	428
HHL	251	177	38,0	95	364	273	92	0.25	428
HHH	318	109	21,3	68	368	177	191	0.52	427
CCC1	249	181	37,9	94	366	276	90	0.25	431
CCC2	225	204	31,9	72	365	276	89	0.24	429
CCC3	244	185	28,7	70	365	255	110	0.30	429